

Properties and applications of metastable precious metal intermetallic compounds

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Certificate of original authorship

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Supitcha Supansomboon

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Table of Contents

| | |
|--|------|
| Certificate of original authorship | i |
| Acknowledgements | ii |
| Table of Contents | v |
| Abstract | viii |
| Publications and conference presentations arising from this work | x |
| List of Figures | xii |
| List of Tables | xxii |
| Chapter 1: Introduction | 1 |
| Chapter 2: Literature review | 6 |
| 2.1 General: precious metal alloys and intermetallic compounds | 7 |
| 2.1.1 Definition of precious metal alloys and intermetallic compounds | 7 |
| 2.1.2 Applications of precious metals and their alloys and intermetallic compounds | 8 |
| 2.2 Optical properties of materials | 13 |
| 2.2.1 The colour of metallic materials | 13 |
| 2.2.2 The CIE-L*-a*-b* colour coordinate system | 14 |
| 2.2.3 Dielectric function | 15 |
| 2.2.4 Plasmon resonances in precious metal nanoparticles | 17 |
| 2.3 Specific precious metal alloys | 18 |
| 2.4 Specific precious metal intermetallic compounds | 22 |
| 2.4.1 Colour of pure phases | 22 |
| 2.4.2 Alloying effects | 27 |
| 2.5 Nanoporous precious metal sponges | 29 |
| 2.5.1 Nanoporous gold (np-Au) | 32 |
| 2.5.2 Nanoporous silver (np-Ag) | 33 |
| 2.5.3 Nanoporous platinum (np-Pt) | 34 |
| 2.5.4 Nanoporous palladium (np-Pd) | 35 |

| | |
|---|-----|
| Chapter 3: General Experimental | 37 |
| 3.1 Overview | 38 |
| 3.2 Materials preparation | 39 |
| 3.2.1 Magnetron sputtering | 39 |
| 3.2.2 Heat treatment | 41 |
| 3.3 Materials characterization | 42 |
| 3.3.1 X-ray diffraction | 42 |
| 3.3.2 Scanning Electron Microscopy (SEM) | 46 |
| 3.3.3 Transmission Electron Microscopy (TEM) | 47 |
| 3.3.4 Determination of optical properties | 50 |
| Chapter 4: The AuAl ₂ -PtAl ₂ system | 53 |
| 4.1 Background | 54 |
| 4.1.1 Review of the fabrication and applications of AuAl ₂ and PtAl ₂ | 54 |
| 4.1.2 Review of the optical properties of AuAl ₂ and PtAl ₂ | 59 |
| 4.2 Objective of this chapter | 63 |
| 4.3 Experimental details specific to this chapter | 63 |
| 4.4 Results and discussion | 65 |
| 4.4.1 Single layer films of coloured intermetallic compounds | 65 |
| 4.4.2 Bi-layers of coloured intermetallic compounds | 85 |
| 4.4.3 Multi-layer films of coloured intermetallic compounds | 88 |
| 4.5 Conclusion | 117 |
| Chapter 5: Nanoporous platinum sponges | 119 |
| 5.1 Background | 120 |
| 5.2 Objectives of this chapter | 127 |
| 5.3 Experimental detail specific to this chapter | 127 |
| 5.4 Results and discussion | 130 |
| 5.4.1 Effect of composition | 130 |

| | |
|---|-----|
| 5.4.2 Effect of temperature | 137 |
| 5.4.3 Effect of deposition time | 144 |
| 5.4.4 Effect of deposition rate | 145 |
| 5.4.5 Effect of de-alloying parameters | 149 |
| 5.4.6 Comparison between my nanoporous Pt sponges and those in the literature | 150 |
| 5.5 Conclusion | 157 |
| Chapter 6: Conclusions and future work | 158 |
| 6.1 The AuAl ₂ -PtAl ₂ system | 159 |
| 6.2 Nanoporous platinum sponges | 161 |
| References | 163 |

Abstract

Precious metal alloys and compounds have myriad applications in the fast-expanding horizons of the commercial and industrial worlds. They are also fascinating topics for scientific research. These materials have a long history, with gold and silver amongst the very earliest metals used by humans. Over the past millennia, the primary applications of the precious metals and their alloys have been in the ever-lucrative jewellery manufacturing industry. The traditional alloys have been perfected in over three thousand years of experience. However, in the recent past, precious metal alloys and compounds have also found themselves a crucial place of pride in the burgeoning ‘advanced materials’ sector. Gold-based and platinum-based alloys and compounds are amongst the candidates being investigated for serving in those applications. In the present project I sought to explore how gold aluminide and platinum aluminide could be developed for further innovative applications. In particular, I initially became interested in the optical properties of these materials, with a view to developing their application in the jewellery industry. The Pt_xAl alloys are, however, also useful as precursors for producing nanoporous metal sponges. The availability of such samples from the first part of the project encouraged me to consider technological applications of the aluminides in the chemical catalysis industry in the second part of the project. The two parts are linked by virtue of starting with the same materials, which are fabricated and mostly characterized the same way. In both cases the samples are fabricated as thin films by direct-current magnetron sputtering and then various techniques are used to characterize their chemical composition, structures, morphologies and specific properties. The main difference comes only at the very end of each part, with the first group of materials being evaluated on their optical properties and the second on their sponge-forming properties.

My work is developed around two hypotheses. First, I hypothesized that the compounds PtAl_2 (brassy yellow) and AuAl_2 (metallic purple) can be alloyed to yield a range of intermediate colours. It is generally stated that these compounds would be immiscible but I proposed that a series of metastable solid solutions could be formed by means of magnetron sputtering. Secondly, I hypothesised that the preparation of nanoporous platinum sponges from metastable (Pt_xAl) precursors would produce a different result than producing them from well-crystallized precursors, and that this could be exploited to provide a new way to control the morphology of such sponges.

The work has showed that the attractive colours of the intermetallic compounds AuAl_2 (‘purple gold’) and PtAl_2 (‘golden platinum’) can be combined or mixed to produce an interesting colour spectrum. This may be of interest to the jewellery industry. A series of metastable solid solutions could be formed by using the magnetron sputtering technique, which enables users to produce any desired stoichiometry. In addition, procedures to reliably

produce pure AuAl_2 and PtAl_2 thin films have been established. These have lattice parameters of 0.599 nm and 0.594 nm respectively, which are similar to those of bulk samples produced by vacuum arc melting. Addition control may be obtained by designing multilayer stacks of these intermetallic compound films, with both bi-layer and multi-layer films being produced in the present project. It was also shown that a metastable solid solution of Au and Pt could be formed by sputtering, with a co-deposited film of 54 at.%Au- 46 at.%Pt film forming a solid solution with a lattice parameter of 0.401 nm, which lies between that of pure Au films (0.408 nm) and pure Pt films (0.394 nm). This metastable solid solution could be reacted with a pure Al film to form a metastable solid solution of $(\text{Au,Pt})\text{Al}_2$ after annealing. However, thin film stacks of AuAl_2 and PtAl_2 may be a better choice to tune colours of these two compounds as they are easier to control.

Next I showed that Pt-Al alloys and intermetallic compounds can be de-alloyed in alkaline solutions to produce nanoporous platinum sponges. These nanoscale sponges can be used as chemical catalysts although I did not pursue this aspect myself. Rather, in this part of the project I considered how the microstructure of the precursor alloys could control the morphology of subsequent sponges. Once again, metastable precursors could be prepared by using magnetron sputtering, and produced a different morphology of sponges compared to those produced from well-crystallized precursors. Other processing parameters have also been studied. It was found that mole fraction (χ_{Al}) of Al in the precursor and the deposition temperature are the two most important factors. Precursors with $\chi_{\text{Al}} < 0.60$ did not form sponges after either deposition at elevated or room temperature. 'Mud-cracked' mesoporous sponges could be formed by preparing precursors with $\chi_{\text{Al}} = 0.67$ and deposited at elevated temperature. The $\text{Pt}_8\text{Al}_{21}$ and meta-stable phase (ϵ -phase) were formed in precursors with $0.67 < \chi_{\text{Al}} < 0.90$ that had been deposited at elevated temperature. In this case de-alloying produced classic isotropic fibrous sponges. Disordered and fragile masses were obtained when precursors with $\chi_{\text{Al}} > 0.90$ were de-alloyed. These had originally consisted of a mixture of PtAl_6 and pure Al. It was also found that precursors that had been deposited at room temperature produced very different sponge morphologies to those that had been deposited at elevated temperature: in this case the amorphous precursors with $0.67 < \chi_{\text{Al}} < 0.96$ produced sponge morphologies ranging from pinhole to unusual isotropic foamy. This work has shown that different morphologies of nanoporous platinum sponges can be produced by controlling the processing parameters. These sponges might be considered for use in specific catalytic or sensor applications because they can be fabricated using simple and cost-effective production techniques.

Publications and conference presentations arising from this work

Publications

1. Supansomboon, S., Bhatia, V., Thorogood, G., Dowd, A., and Cortie, M.B., Advanced precious metal alloys, *Materials Australia*, 2011. 44 (4): p.41-46.
2. Keast, V.J., Birt, K., Koch, C.T., Supansomboon, S., and Cortie, M.B., The role of plasmons and interband transitions in the color of AuAl₂, AuIn₂, and AuGa₂. *Applied Physics Letters*, 2011. **99**(11): p. 111908.
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List of Figures

| | |
|--|----|
| Figure 1.1 Periodic table of elements | 2 |
| Figure 1.2 Crystal structure of precious metals (a) face-centered cubic (FCC) and (b) close-packed hexagonal (HCP) [4]..... | 3 |
| Figure 2.1 Schematic representation of the mechanism of photon absorption (a) and emission (b) for metallic materials [35] | 14 |
| Figure 2.2 CIE $L^*a^*b^*$ colour space [38]..... | 15 |
| Figure 2.3 Imaginary part of the interband dielectric constant as function of energy (a) Au-Ag and (b) Au-Cu [39]..... | 16 |
| Figure 2.4 Imaginary part of the interband dielectric constant and energy of Ag-Cu series (a) Cu-rich and (b) Ag-rich [39]..... | 17 |
| Figure 2.6 Relationship between colour and composition in the Au-Ag-Cu system[62]..... | 19 |
| Figure 2.7 Comparison of coloured rings from different precious metal alloys [61] | 20 |
| Figure 2.8 Reflectivity curves of gold and its alloys (a) gold-silver alloys and (b) gold-palladium alloys [63] | 22 |
| Figure 2.9 Crystal structures of coloured binary intermetallic compounds (a) Caesium chloride structure and (b) Calcium fluoride (Courtesy CrystalMaker Software Ltd, UK)..... | 23 |
| Figure 2.10 Reflectivity curves of coloured gold intermetallic compounds: AuAl ₂ (curve 1), AuIn ₂ (curve 2) and AuGa ₂ (curve 3) [63]..... | 24 |
| Figure 2.11 CIE a^* and b^* colour coordinates of alloys along the 18 carat pseudo-binary, and position of phase fields [70]..... | 29 |
| Figure 2.12 Classification of nanoporous metals[76] | 31 |
| Figure 2.13 Nanoporous gold by dealloying Au-Ag (a) Model for dealloying [7], (b) SEM micrograph of nanoporous gold by dealloying Au-Ag in nitric acid [89] and (c) Simulated porous structure of nanogold which made from Au _{0.35} Ag _{0.65} precursor [90] | 32 |
| Figure 2.14 Nanoporous silver generated from Ag-Al precursors (a) α -Al rich region and (b) α -Al and Ag ₂ Al region [116] | 34 |
| Figure 2.15 Nanoporous platinum produced by co-sputtered Pt _x Si _{1-x} amorphous film for different initial compositions (a) Pt _{0.10} Si _{0.90} as deposited (b) isotropic open-cell foam (c) Pt _{0.34} Si _{0.66} as deposited (d) anisotropic columnar-type foam (e) Pt _{0.33} Si _{0.67} as deposited and (f) anisotropic Voronoi [133]..... | 35 |
| Figure 2.16 Nanoporous palladium by dealloying in various precursors (a) Pd-Co [146] (b) Pd-Ni [139] and (c) Pd-Cu [142] | 36 |

| | |
|--|----|
| Figure 3.1 A schematic diagram of magnetron sputtering mechanism | 39 |
| Figure 3.2 Relationship between sputter yield and atomic number of elements for argon ion energy at 400 eV [155] | 40 |
| Figure 3.3 A co-deposition technique during sputtering process, photograph taken during the present project..... | 40 |
| Figure 3.4 Tube furnace for post-deposition annealing treatment..... | 41 |
| Figure 3.5 Schematic of an X-ray diffractometer in the Bragg-Brentano configuration [156] | 43 |
| Figure 3.6 Schematic diagram of XRD (a) conventional θ - 2θ geometry and (b) grazing angle geometry [160]..... | 44 |
| Figure 3.7 (a) High temperature furnace and (b) platinum heater bar with cavity [165] | 45 |
| Figure 3.8 Information in powder diffraction pattern [167] | 45 |
| Figure 3.9 A field emission scanning electron microscope (Zeiss Supra 55VP)..... | 47 |
| Figure 3.10 Cross section preparation for TEM (a) schematic of stack sample prepared using the sandwich technique and (b) Interface of thin film after polishing with diamond of 1 μm (the arrow indicate the location of the glue line) [175] | 49 |
| Figure 3.11 An optical model of a thin film sample [177] | 51 |
| Figure 3.12 Diagram of the process for ellipsometry data analysis [178] | 52 |
| Figure 4.1 Phase diagram of Al-Au system by Okamoto, H.(1991) [182]..... | 54 |
| Figure 4.2 Phase diagram of Al-Pt system by McAlister, A.J. and Kahan, D.J.(1986) [182]. | 55 |
| Figure 4.3 Purple gold by investment casting (Courtesy JARAD Project by Srinakharinwirot University, Bangkok Fashion City under the Ministry of Industry of Thailand, Thailand) | 56 |
| Figure 4.4 AuAl ₂ - carat purple gold (top row) and AuIn ₂ - blue gold (bottom row) (Courtesy Co. Reischauer GmbH, Idar Oberstein, Germany) [6]..... | 56 |
| Figure 4.5 Bi-metal casting (a) 950 Pd casting with injected wax for the 2nd bi-metal casting process step and (b) Bi-metal castings of 14k blue gold (left) and 18k purple gold (right) with 950 Pd (Courtesy Vendorafa-Lombardi Srl, Valenza, Italy) [6] | 57 |
| Figure 4.6 Purple gold by powder metallurgy process (Courtesy Lee Hwa Jewellery, Singapore) [186] | 57 |
| Figure 4.7 Purple glory gemstone-like AuAl ₂ casting in setting on ring (courtesy M.B Cortie) [180]..... | 57 |
| Figure 4.8 Platigems and Platigem jewellery (Courtesy Mintek, South Africa) [187]..... | 58 |

| | |
|---|----|
| Figure 4.9 AuAl ₂ -coated items made by depositing onto sterling silver costume jewellery by the present author [181] | 58 |
| Figure 4.10 Reflectivity of gold intermetallic compounds from experiment (solid curve) and calculation (dashed curved) [191]..... | 60 |
| Figure 4.11 Dielectric function of gold intermetallic compounds; ϵ_1 (solid curve) and ϵ_2 (dashed curved) [191] | 60 |
| Figure 4.12 Dielectric function of ordered intermetallic compounds [192] | 61 |
| Figure 4.13 Reflectivity of ordered intermetallic compounds comparing with experimental reflectivity of PtAl ₂ thin film [192] | 61 |
| Figure 4.14 Comparison CIE Lab colour coordinates of AuAl ₂ , Au _{0.5} Pt _{0.5} Al ₂ , Au _{0.25} Pt _{0.75} Al ₂ and PtAl ₂ [192]..... | 61 |
| Figure 4.15 CIE L*a*b* colour gamut of Au-Ni-Au tri layer in reflection [203]..... | 62 |
| Figure 4.16 Deposition rate of aluminium, gold and platinum as function of current | 64 |
| Figure 4.17 X-ray patterns of Pt-Al compound films by co-sputtering using varying current level of aluminium, PtAl ₂ are formed by using current at 0.395 A (yellow pattern) | 66 |
| Figure 4.18 Morphology of Pt-Al compound films (a) PtAl ₄₀₀ (b) PtAl ₃₉₅ (c) PtAl ₃₆₀ and (d) PtAl ₃₃₅ | 67 |
| Figure 4.19 Comparison of reflectance spectra of PtAl ₂ in bulk and film | 68 |
| Figure 4.20 Comparison of morphology of surfaces of PtAl ₂ in (a) bulk and (b) film | 68 |
| Figure 4.21 Comparison of X-ray patterns of PtAl ₂ in bulk and film..... | 69 |
| Figure 4.22 X-Ray patterns of Au-Al compounds..... | 70 |
| Figure 4.23 Morphologies of Au-Al films produced by using different power levels on the gold target (a) 16 W (sample AuAl ₀₄₀) in low magnification, (b) 16 W (sample AuAl ₀₄₀) in high magnification, (c) 26 W (sample AuAl ₀₆₀) in low magnification, (d) 26 W (sample AuAl ₀₆₀) in high magnification and (e) 21 W (sample AuAl ₀₅₀) | 71 |
| Figure 4.24 Reflectance spectra of Au-Al compounds | 72 |
| Figure 4.25 Comparison of X-Ray patterns of AuAl ₂ , deposited at different temperature | 73 |
| Figure 4.26 Microstructure of AuAl ₂ films, deposited at different temperatures (a) below 400 °C and (b) at 400 °C | 73 |
| Figure 4.27 Comparison of reflectance spectra of AuAl ₂ in bulk and film | 74 |
| Figure 4.28 Morphologies of AuAl ₂ bulk sample by (a) SEM and (b) LM..... | 74 |

| | |
|---|----|
| Figure 4.29 Morphologies of AuAl ₂ thin film (a) plan view and (b) cross-section..... | 75 |
| Figure 4.30 X-ray patterns of AuAl ₂ in bulk and thin film samples..... | 75 |
| Figure 4.31 Diagram illustrating the process for fabricating coloured intermetallic compounds by controlling the chemical composition and thickness of (a) PtAl ₂ film and (b) AuAl ₂ film | 76 |
| Figure 4.32 Cross-sections of the thin films of the binary intermetallic compounds after annealing at 400 °C (a) AuAl ₂ and (b) PtAl ₂ | 76 |
| Figure 4.33 X-ray patterns of colour intermetallic compounds in different thicknesses of film (a) PtAl ₂ films and (b) AuAl ₂ films | 77 |
| Figure 4.34 Reflectance (R) and transmittance (T) spectra of PtAl ₂ films (Exp) with model fitted (Model Fit) to different thicknesses of film (a) 100 nm and (b) 40 nm | 78 |
| Figure 4.35 Reflectance and transmittance spectra of AuAl ₂ films with model fitted to different thicknesses (a) 100 nm and (b) 40 nm | 79 |
| Figure 4.36 Dielectric functions of coloured intermetallic compounds by reflectance and transmission data (a) PtAl ₂ and (b) AuAl ₂ | 80 |
| Figure 4.37 Colour of simulated thin films in CIE L*a*b* space, with the colour of each film rendered into the surface of a spherical data point. Both reflectance (yellow) and transmittance (grey) modes are shown for the different thicknesses (a) front view (b) top view and (c) perspective view | 82 |
| Figure 4.38 Colour of simulated thin films in CIE L*a*b* space, with the colour of each film rendered into the surface of a spherical data point. Both reflectance (purple) and transmittance (yellow-green) mode in different thickness of film are shown (a) front view (b) top view and (c) perspective view | 83 |
| Figure 4.39 Dielectric functions of coloured intermetallic compounds found by analysis of ellipsometric data (a) PtAl ₂ and (b) AuAl ₂ | 84 |
| Figure 4.40 The two kinds of bi-layer films produced (a) AuAl ₂ /PtAl ₂ and (b) PtAl ₂ /AuAl ₂ | 85 |
| Figure 4.41 The reflectance spectra of bi-layers of AuAl ₂ /PtAl ₂ | 85 |
| Figure 4.42 Cross-section of bi-layers films of PtAl ₂ /AuAl ₂ before annealing (a) In lens mode and (b) backscatter mode | 86 |
| Figure 4.43 Cross-section of PtAl ₂ /AuAl ₂ film after annealing under vacuum at 400 °C (a) for 24 hours and (b) for 48 hours..... | 86 |
| Figure 4.44 Calculated reflectance (a) and colour (b) of 200 nm PtAl ₂ film that has been over-coated with indicated thickness of AuAl ₂ | 87 |

| | |
|--|----|
| Figure 4.45 Calculated reflectance (a) and colour (b) of 200 nm AuAl_2 film that has been over-coated with indicated thickness of PtAl_2 | 87 |
| Figure 4.46 Schematic illustration of the arrangements of the four-layer films of Al-Au-Pt (a) Au on the top and (b) Pt on the top | 88 |
| Figure 4.47 Cross-sections of four-layer films of Al-Au-Pt with Au on the top, as deposited at 25 °C (a) In lens and (b) RBSD | 89 |
| Figure 4.48 Cross-sections of four-layer films of Al-Au-Pt with Au on the top, after annealing at 400 °C (a) SEM:In lens mode (b) SEM:RBSD mode and (c) TEM | 90 |
| Figure 4.49 Cross-sections of four-layer films of Al-Au-Pt with Pt on the top, after annealing at 400 °C (a) SEM and (b) TEM | 90 |
| Figure 4.50 The reflectance spectra from the front side of a four-layered film of Al-Au-Pt (Au on the top) as deposited at 25 °C before and after annealing. Data for a pure gold film of 30 nm thickness is shown for comparison | 91 |
| Figure 4.51 The reflectance spectra from the back side of the above four-layered film, before and after annealing | 92 |
| Figure 4.52 The reflectance spectra from the front side of a four-layered film of Al-Au-Pt (Pt on the top) as depositing at 25 °C before and after annealing. Data for a pure platinum thin film of 30 nm thickness is shown for comparison | 92 |
| Figure 4.53 The reflectance spectra from the back side of the above four-layered film, before and after annealing | 93 |
| Figure 4.54 X-ray patterns of four-layer films of AlAuPt comparing the structure before and after annealing at 400 °C (a) pure gold layer on the top and (b) pure platinum layer on the top (both were deposited at 25 °C), with patterns for AuAl_2 and PtAl_2 films shown for comparison | 94 |
| Figure 4.55 The arrangement of the six-layered films (a) Al-Au-Pt and (b) Al-Au | 95 |
| Figure 4.56 Cross-section views of the six-layer film of Al-Au-Pt after annealing at 400 °C (a) SEM-In lens (b) SEM-RBSD and (c) TEM | 96 |
| Figure 4.57 The reflectance spectra of the top of the six-layer film of Al-Au-Pt (Pt on the top) after annealing | 96 |
| Figure 4.58 The X-ray pattern of the six-layer film of Al-Au-Pt after annealing, with patterns for PtAl_2 and AuAl_2 films shown for comparison | 97 |
| Figure 4.59 Cross-sections of six-layer films of Al-Au (a) before annealing-In lens, (b) before annealing – RBSD, (c) after annealing at 400 °C – In lens and (d) after annealing at 400 °C – RBSD | 97 |

| | |
|---|-----|
| Figure 4.60 The X-ray pattern of the six-layer film of Al-Au before and after annealing, with patterns for AuAl ₂ films shown for comparison | 98 |
| Figure 4.61 The different arrangements of eight-layer films of Al-Au-Pt (a) 50 nm each layer, Au on the top and (b) 50 nm each layer, Pt on the top | 98 |
| Figure 4.62 Cross-sectional views of eight-layered films of Al-Au-Pt (a) before annealing-In lens, (b) before annealing – RBSD, (c) after annealing at 400 °C – In lens and (d) after annealing at 400 °C – RBSD | 99 |
| Figure 4.63 The X-ray pattern of eight multi-layers films of Al-Au-Pt (Pt on the top) after annealing, comparing with PtAl ₂ film..... | 100 |
| Figure 4.64 The reflectance spectrum of the surface of eight multi-layers films of Al-Au-Pt (Pt on the top) after annealing, comparing with a single PtAl ₂ film..... | 100 |
| Figure 4.65 The morphologies of eight multi-layer films of Al-Au-Pt which Au on the top after annealing at 400 °C (a) cross-sectional area and (b) surface area | 101 |
| Figure 4.66 The X-ray pattern of the eight-layered films of Al-Au-Pt (Au on the top) after annealing. A pattern for a simple AuAl ₂ film is shown for comparison..... | 101 |
| Figure 4.67 The reflectance spectrum of the surface of the eight-layer film of Al-Au-Pt (Au on the top) after annealing, in comparison to that of a simple, single-layer AuAl ₂ film..... | 102 |
| Figure 4.68 The arrangement of eight-layered films of Al-Au-Pt with each layer being 25 nm thick (Au on the top) | 102 |
| Figure 4.69 The X-ray patterns of the eight-layered sample produced with half the deposition time of the standard eight-layered sample of Al-Au-Pt (Au on the top), both before and after annealing, compared with that of a simple, single-layer AuAl ₂ film..... | 103 |
| Figure 4.70 The cross-sectional view of the eight-layer films of Al-Au-Pt in which layer thickness was halved, (a) before annealing and (b) after annealing at 400 °C for 30 minute | 104 |
| Figure 4.71 Average integrated peak areas of PtAl ₂ and/or AuAl ₂ over the (111), (200), (220) and (311) peaks as a function of temperature | 105 |
| Figure 4.72 Peak area of four layers stack formed by depositing pure metals at (111) of PtAl ₂ and AuAl ₂ | 105 |
| Figure 4.73 The design of stacks consisting of co-deposited precious metals and aluminium (a) precious metals on the bottom (Al/(Au,Pt)), (b) precious metals on the top ((Au,Pt)/Al) and (c) co-depositing precious metals on the top but with half the thickness | 106 |
| Figure 4.74 A comparison of X-ray patterns of thin films of (Au,Pt) solid solution to those pure Au and pure Pt | 107 |

| | |
|--|-----|
| Figure 4.75 X-ray patterns of different arrangements of stacks made of a layer of co-deposited Au and Pt, and Al, before and after annealing | 108 |
| Figure 4.76 X-ray patterns of an Al/(Au,Pt) sample, followed by annealing at various temperatures..... | 108 |
| Figure 4.77 Comparison of X-ray patterns of an Al/(Au,Pt) sample, followed by annealing at 400 °C and 500 °C | 109 |
| Figure 4.78 Comparison of the X-ray diffraction patterns obtained after annealing the stacks with 20, 60 and 120 nm of (Au,Pt) at 400 °C | 110 |
| Figure 4.79 X-ray patterns of a mixed AuAl ₂ /PtAl ₂ sample formed by co-depositing Au and Pt onto Al. The fitted pattern was obtained by Rietveld refinement on a PtAl ₂ structure | 111 |
| Figure 4.80 Cross-section of the Al/(Au,Pt) sample with 20 nm of co-deposited (Au,Pt) with EDS elemental scan and mapping..... | 112 |
| Figure 4.81 High resolution TEM images of the Al/(Au,Pt) sample with 20 nm of co-deposited (Au,Pt) (a) top layer and (b) bottom layer | 113 |
| Figure 4.82 The reflectance spectra of the 65 at.% Al-23 at.% Pt-12 at.% Au sample on its front and back sides, compared with the front side of the sample before annealing and that of a pure PtAl ₂ film | 114 |
| Figure 4.83 The reflectance spectra of 56 at.% Al-22 at.% Pt-22 at.% Au on its front and back sides, compared with the front side of the sample before annealing and a pure AuAl ₂ film. | 114 |
| Figure 4.84 X-ray diffraction patterns of samples made by co-depositing Au and Pt on top of an Al layer (a) 65 at.% Al - 23 at.% Pt - 12 at.% Au and (b) 56 at.% Al - 22 at.% Pt - 22 at.% Au. Data for before and after annealing, and for pure PtAl ₂ and pure AuAl ₂ is shown | 115 |
| Figure 4.85 Lattice parameter and peak area of Al/(Au,Pt) sample as a function of temperature (a) Lattice parameter of (Au,Pt)Al ₂ in Al/(Au,Pt) sample and (b) peak area of (Au,Pt)Al ₂ phase (111) and Pt ₂ Al ₃ (002) | 117 |
| Figure 5.1 Various techniques for nanoporous platinum fabrication [207] | 120 |
| Figure 5.2 Pt-Al phase diagram [237]..... | 121 |
| Figure 5.3 The different lattice types of the intermetallic compounds in the Pt-Al binary system [229] | 122 |
| Figure 5.4 Effect of Al content on structure of sponges produced from precursors with $\chi_{Al} > 0.80$ (a) X-ray diffraction pattern of increasing amount of Al, (b) X-ray diffraction patterns of de-alloyed Pt sponges (c) and (d) SEM micrograph of isotropic foamy Pt sponge from precursor with $\chi_{Al} = 0.88$ and 0.85 respectively (e) TEM micrograph of Pt sponge from precursor with $\chi_{Al} = 0.88$ [239] | 124 |

| | |
|--|-----|
| Figure 5.5 Simulation of the de-alloying of the sponges by using Monte Carlo model as a function of χ_{Al} (a) Morphologies of sponges in various aluminium content (b) Ratio of surface atoms to total atoms of sponges (v) and χ_{Al} remaining in sponge. (c) Average mean and Gaussian curvatures of sponges. (d) Effect of Lennard-Jones temperature on the de-alloying of a starting alloy with $\chi_{Al} = 0.80$. This work was performed by my co-authors [239]..... | 125 |
| Figure 5.6 Three distinct morphologies of nanoporous platinum as correlated with co-sputtering parameter, initial alloy composition and thickness [133] | 126 |
| Figure 5.7 Effect of de-alloying system on ligament size of nanoporous platinum from different alloy systems (a) ligament sizes of different noble metal-aluminium with de-alloying with 5% HCl and 20% NaOH and (b) ligament sizes of platinum-gold-copper alloys with varying noble metal content..... | 126 |
| Figure 5.8 Nanoporous platinum produced from $Pt_{0.20}Cu_{0.80}$, then de-alloyed in 93% H_2SO_4 and coarsened at different temperatures (a) 250 °C (b) 300 °C (c) 400 °C and (d) 500 °C [246]..... | 127 |
| Figure 5.9 De-alloying process on Pt-Al precursor (a) Bubble of H_2 on Pt-Al precursor immersing in alkali solution and (b) model of aluminium removing from Pt-Al precursor [239]..... | 128 |
| Figure 5.10 Flowchart showing preparation of Pt-Al precursors and the subsequent nanoporous platinum..... | 129 |
| Figure 5.11 Pt-Al precursor film deposited at 400 °C with $\chi_{Al} \approx 0.50$ (a) XRD patterns comparing with other phases from calculated and database and (b) SEM micrograph after de-alloying showing that a nanoporous sponge did not form | 130 |
| Figure 5.12 Pt-Al precursor film deposited at 400 °C with $\chi_{Al} \approx 0.60$ (a) XRD patterns comparing with Pt_2Al_3 from database (b) SEM micrograph before de-alloying (c) SEM micrograph after de-alloying..... | 131 |
| Figure 5.13 Pt-Al precursor film deposited at 400 °C with $\chi_{Al} = 0.67$ (a) XRD patterns comparing with Pt_2Al_3 from database and (b) reflectance spectra | 132 |
| Figure 5.14 ‘Mud-cracked’ sponges produced by de-alloying sample with $\chi_{Al} = 0.67$ (a) a porous and cracked film (b) cross-sectional view and (c) curled up porous and cracked film at low magnification | 132 |
| Figure 5.15 TEM micrographs of de-alloyed samples with $\chi_{Al} = 0.67$ | 133 |
| Figure 5.16 Pt-Al precursor film with $0.67 < \chi_{Al} < 0.80$ (a) XRD patterns of precursors with $\chi_{Al} = 0.78$ (deposited at 400 °C) and precursors with $\chi_{Al} = 0.75$ (deposited at room temperature then crystallized by heating ~400 °C), comparing with Pt_8Pt_{21} from database and reported ϵ phase (b) crystallization of ϵ phase at ~360 °C on heating up precursor with $\chi_{Al} = 0.75$ (c) morphology of Pt-Al precursor with $\chi_{Al} = 0.78$ as deposited (d) SEM micrograph of | |

| | |
|---|-----|
| isotropic fibrous sponges in plain view and (e) SEM micrograph of isotropic fibrous sponges in cross-sectional view | 134 |
| Figure 5.17 Pt-Al precursor film deposited at 400 °C with $\chi_{Al} = 0.82$ (a) (a) XRD patterns comparing with Al-rich phases from database and ϵ phase (b) and (c) SEM micrograph of isotropic fibrous sponges | 135 |
| Figure 5.18 Pt-Al precursor film deposited at 400 °C with $\chi_{Al} > 0.90$ (a) XRD pattern comparing with PtAl ₆ and Al from database (b) SEM micrograph as deposited (c) SEM micrograph after de-alloying (d) TEM de-alloying and (e) High resolution TEM after de-alloying | 136 |
| Figure 5.19 XRD patterns of the precursors were deposited at room temperature with $\chi_{Al} = 0.67$ | 137 |
| Figure 5.20 Morphology of partially de-alloyed sponges produced from the precursors were deposited at room temperature with $\chi_{Al} = 0.67$ (a) plan view and (b) cross-sectional view .. | 138 |
| Figure 5.21 Morphology of sponge produced from a precursor with $\chi_{Al} \approx 0.75$ that had been deposited at room temperature | 138 |
| Figure 5.22 Morphology of Pt-Al precursors, deposited at room temperature with $\chi_{Al} > 0.80$ (a) as deposited (b) $\chi_{Al} \approx 0.83$ after de-alloying (c) $\chi_{Al} \approx 0.88$ after de-alloying (d) $\chi_{Al} \approx 0.96$ after de-alloying and (e) curled up porous Pt sponge and shown cross-sectional view | 139 |
| Figure 5.23 TEM mapping on Pt-Al precursors, deposited at room temperature with $\chi_{Al} = 0.92$ | 140 |
| Figure 5.24 TEM-EDS analysis through the cross-sectional area of Pt-Al precursors, deposited at room temperature with $\chi_{Al} = 0.92$. The presence of Cu is due to redeposited materials during PIPS | 140 |
| Figure 5.25 Distribution of pore sizes from Pt-Al precursor with different mole fraction of Al (a) $\chi_{Al} = 0.83$ (b) $\chi_{Al} = 0.88$ and (c) $\chi_{Al} = 0.96$ | 141 |
| Figure 5.26 TEM micrograph of sponge formed from precursor with $\chi_{Al} \approx 0.88$ (a) a continuous network of Pt surrounding the void and (b) lattice fringe image at high resolution | 142 |
| Figure 5.27 Comparison of X-ray diffraction pattern between samples with $\chi_{Al} > 0.80$, which were deposited at room temperature and above 400 °C and the sample with $\chi_{Al} = 0.82$, which was deposited at elevated temperature | 143 |
| Figure 5.28 Morphologies of samples with $\chi_{Al} > 0.80$, which were deposited at room temperature, then annealed at various temperatures followed by de-alloying process in alkali solution (a) as deposited at room temperature (b) annealed at 100 °C (c) annealed at 200 °C (d) annealed at 300 °C (e) annealed at 400 °C and (f) annealed at 500°C | 144 |

| | |
|--|-----|
| Figure 5.29 Morphologies of samples with $\chi_{Al}=0.83$, which were deposited at room temperature with various deposition times (a) 5 minutes (b) 10 minutes and (c) 30 minutes | 145 |
| Figure 5.30 Pinhole sponge produced from precursors that deposited at room temperature with high deposition rate of Pt in various Al contents (a) $\chi_{Al} \approx 0.62$ (b) $\chi_{Al} \approx 0.67$ and (c) $\chi_{Al} \approx 0.69$ and (d) preferential dissolution along grain boundaries | 146 |
| Figure 5.31 Foamy sponge produced from precursors that deposited at room temperature with high deposition rate of Pt in various Al contents (a) $\chi_{Al} \approx 0.71$ (b) $\chi_{Al} \approx 0.74$ (c) $\chi_{Al} \approx 0.77$ and (d) view of interior of sponge through walls of crack | 147 |
| Figure 5.32 Morphologies of samples that deposited at room temperature with current level of Pt at 0.005 A (a) partly foamy sponges and (b) fragile sponges..... | 148 |
| Figure 5.33 Morphologies of samples that deposited at room temperature with current level of Pt at 0.025 A (a) foamy sponges and (b) transparency foamy sponges film | 148 |
| Figure 5.34 Morphologies of samples that deposited at room temperature with different current level of Pt (a) 0.050 A and (b) 0.075 A | 148 |
| Figure 5.35 Foamy sponges produced from precursors that deposited at room temperature with $\chi_{Al} = 0.96$, then de-alloying by different solutions (a) 0.2M NaOH and (b) 0.2M Na ₂ CO ₃ | 149 |
| Figure 5.36 Foamy sponges from precursors that deposited at room temperature with $\chi_{Al} = 0.92$, then de-alloying by using Na ₂ CO ₃ with different de-alloying times (a) 1 minute (b) 3 minutes (c) 5 minutes (d) 10 minutes and (e) 15 minutes..... | 150 |

List of Tables

| | |
|--|----|
| Table 1.1 Structure and lattice constant of precious metals [1-3]..... | 3 |
| Table 1.2 Selected properties of precious metals [1-3]..... | 4 |
| Table 2.1 Comparison between alloys and intermetallic compounds..... | 7 |
| Table 2.2 Definition of caratage in gold content [1]..... | 9 |
| Table 2.3 Varied content of alloying elements of carat gold alloys for jewellery [12] | 9 |
| Table 2.4 Selected properties and applications of carat gold alloys in jewellery [12] | 10 |
| Table 2.5 Onset of interband transition of selected coloured intermetallic compounds [41, 42] | 17 |
| Table 2.6 Coloured carat gold alloys based on the Au-Ag-Cu system [66] | 21 |
| Table 2.7 Coloured binary intermetallic compounds with CsCl and CaF ₂ structure [68] | 24 |
| Table 2.8 Ternary coloured intermetallic compounds based on a precious metal [68] | 25 |
| Table 2.9 Quaternary coloured intermetallic compounds based on a precious metal [68]..... | 27 |
| Table 2.10 Classification of nanoporous materials and their properties [74] | 30 |
| Table 3.1 Sputter yields (atoms/ion) as a function of argon ion energy of selected metals [154]..... | 40 |
| Table 4.1 Pt-Al films fabricated by co-sputtering using varying currents on the aluminium target. (The current on the platinum target was fixed at 0.125 A or the power was fixed at ~ 55-57 W)..... | 66 |
| Table 4.2 Au-Al films fabricated by co-sputtering using varying current level of gold. (Power of Al was 204 W or current ~0.443-0.452 A)..... | 70 |
| Table 4.3 Quantitative chemical analysis by EDS of Au-Al compounds..... | 70 |
| Table 4.4 Conditions, colour and XRD results of Au-Al films | 72 |
| Table 4.5 A comparison of the CIE XYZ and CIE L*a*b* colour coordinates of thin film and bulk samples of PtAl ₂ and AuAl ₂ | 81 |
| Table 4.6 Deposition conditions for the four-layer films of Al-Au-Pt | 89 |
| Table 4.7 Deposition conditions for the six-layered films of Al-Au-Pt | 95 |
| Table 4.8 Deposition conditions of eight-layer films of Al-Au-Pt. Each layer is 50 nm thick | 99 |

| | |
|--|-----|
| Table 4.9 Deposition conditions of eight-layered film of Al-Au-Pt in which each layer is 25 nm thick | 103 |
| Table 4.10 Chemical composition of a stack of Al/(Au,Pt) with various thicknesses of precious metals, measured after annealing at 400 °C for 60 minutes..... | 110 |
| Table 5.1 List of nanoporous Pt produced by other research works..... | 152 |
| Table 5.2 List of nanoporous Pt produced by this research project..... | 155 |